



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08F 2/40, 2/42		A1	(11) International Publication Number: WO 00/42079
			(43) International Publication Date: 20 July 2000 (20.07.00)
(21) International Application Number: PCT/US00/01291 (22) International Filing Date: 19 January 2000 (19.01.00) (30) Priority Data: 60/116,398 19 January 1999 (19.01.99) US (71) Applicant (for all designated States except US): ANGUS CHEMICAL COMPANY [US/US]; 1500 East Lake Cook Road, Buffalo Grove, IL 60089 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BRUTTO, Patrick, E. [US/US]; 8116 West Winnemac Avenue, Norridge, IL 60656 (US). MOORE, David, W. [US/US]; 8914 Johnson Road, Hebron, IL 60034 (US). HOFFMAN, Marina, D. [US/US]; 784 English Oaks Drive, Cary, IL 60013 (US). (74) Agent: LADD, Thomas, A.; Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(54) Title: STERICALLY-HINDERED ALKYL HYDROXYLAMINES FOR SCAVENGING OF FREE RADICALS			
<div style="text-align: center;"> $\begin{array}{c} R_1 \\ \\ R_2 - C - N - R_4 \\ \quad \quad \\ R_3 \quad \quad OH \end{array} \quad (I)$ </div>			
(57) Abstract			
<p>Free radical scavengers are formed from sterically-hindered alkylhydroxylamines. The free radical scavengers are believed useful to interrupt polymerization reactions or to facilitate storage and transportation of reactive monomers. Free radical scavengers preferably have formula (I).</p>			

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STERICALLY-HINDERED ALKYL HYDROXYLAMINES FOR SCAVENGING OF FREE RADICALS

Free radical scavengers are required in many industrial processes. Examples include free
5 radical polymerizations, such as styrene-butadiene co-polymerizations, where a radical scavenger is
added to stop the reaction prior to complete monomer conversion, and production of unsaturated
monomers where radical scavengers are added to prevent unwanted polymerization.

In free radical polymerizations, it is often desired to stop the reaction before complete
10 monomer-to-polymer conversion. Such "shortstopped" polymers often exhibit superior performance
properties when compared with fully converted polymers. In order to shortstop the reaction, it is
necessary to add a material that will react with the free radicals and prevent them from reforming. Free
radical scavengers serve this purpose. There are many free radical scavengers used commercially as
shortstops. These products suffer from one or more shortcomings. For example, N,N-diethyl-
15 hydroxylamine (DEHA) is effective, however, it is relatively volatile and during steam stripping of
unreacted monomers from emulsion polymers, not enough DEHA remains in the emulsion to completely
stop the reaction. DEHA also contains diethylamine, which can form nitrosamines, which are
undesirable because they have been found to be carcinogenic in laboratory animal studies and are
regulated in some countries. DEHA can be combined with a non-volatile free radical scavenger like
20 sodium dimethyldithiocarbamate (SDD) or sodium tetrasulfide (ST), however, these can create other
problems. SDD can form nitrosamines, while ST can generate toxic, corrosive hydrogen sulfide.
Newer technologies, such as stable free radicals (SFRs), are available which are effective and avoid
many of the above shortcomings. A good example of an SFR is 4-hydroxy-2,2,6,6-
tetramethylpiperidinyloxy, commonly known as 4-hydroxy TEMPO. Although effective, this product is
25 expensive. A need exists, therefore, for a relatively non-volatile, cost effective, non-nitrosamine-
forming free-radical scavenger (shortshop) for radical polymerizations.

In the production of unsaturated monomers, such as styrene, acrylic acid, butadiene, etc.,
there is a tendency for the monomers to polymerize. This results in undesirable fouling of equipment and
30 yield losses. Free radical scavengers are added to such monomer streams during their purification to
prevent such unwanted polymerization. Several scavengers are used commercially, but all suffer from
one or more drawbacks. For example, dinitrophenol (DNP) derivatives are widely used as styrene
stabilizers, however, they are very toxic and can be an explosion hazard under certain conditions.

Phenylenediamine (PD) derivatives are also widely used as stabilizers in styrene and other monomers, however, they require the presence of oxygen for optimum performance. Addition of oxygen to monomer purification equipment can be hazardous and must be closely controlled. Newer chemistries, such as SFRs and N-nitroso-N-phenyl hydroxylamine, ammonium salt (Cupferron), are effective, but are expensive and, in the case of Cupferron, there are safety concerns (toxicity, suspected carcinogen). Accordingly, there is a need for a high boiling, effective monomer stabilizer, which is compatible with a variety of monomers and relatively safe to handle and use.

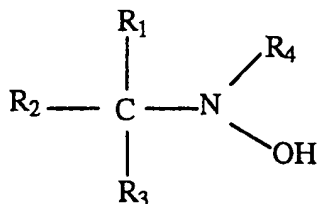
In one aspect, the invention relates to sterically-hindered alkyl hydroxylamines as free radical scavengers for shortstopping radical polymerizations and as inhibitors for preventing unwanted polymerization of unsaturated monomers during their production. Preferred sterically-hindered alkyl hydroxylamines are defined by the formulas below. A particularly preferred compound is t-butyl hydroxylamine. Alternatively, related stable nitroxides may be used.

In another aspect, the invention is an improved process for carrying out free radical polymerization reactions in which a sterically-hindered alkyl hydroxylamine is added as a shortstopping agent. The invention also includes stabilization of monomers, especially styrene, to limit unwanted polymer formation during production or storage and transportation of such monomers.

Shortstops And Inhibitors

The invention includes using sterically-hindered alkyl hydroxylamines as free radical scavengers for shortstopping radical polymerizations and for stabilizing monomers during their production and purification. The preferred sterically-hindered alkyl hydroxylamines of the invention are described by the following Formulas.

Formula I



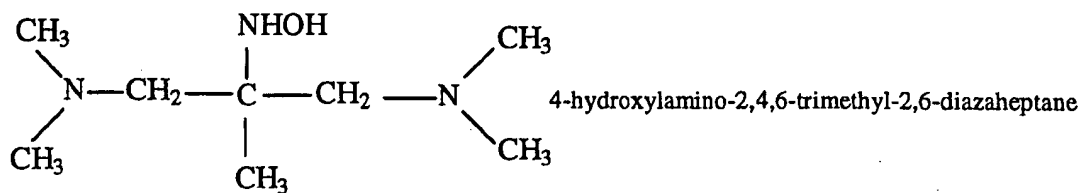
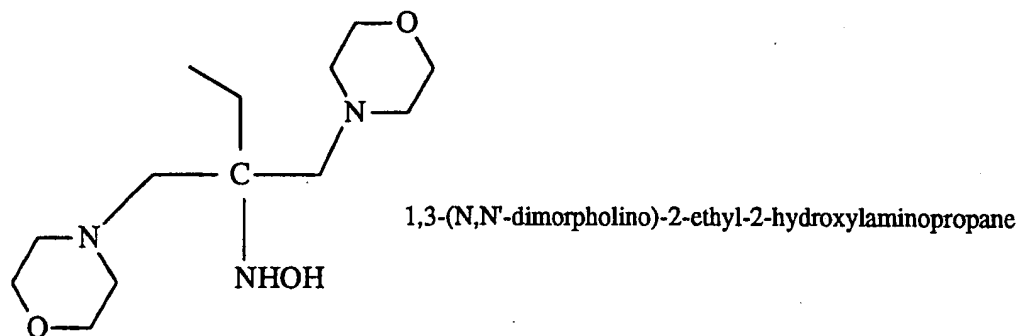
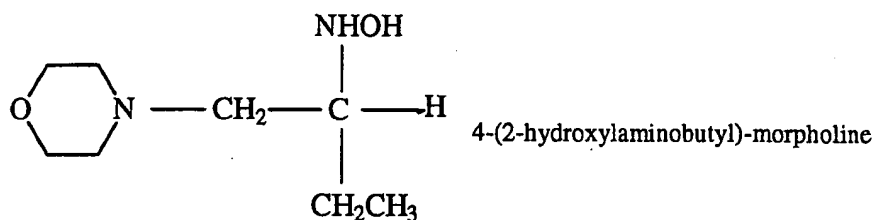
where: R_1 , R_2 , R_3 , and R_4 are independently hydrogen, C_1 - C_{10} alkyl, hydroxyalkyl, or amino alkyl, optionally substituted with a heterocyclic radical, providing that not more than one of R_1 , R_2 and R_3 may be hydrogen; and R_4 is hydrogen or C_1 - C_{10} alkyl

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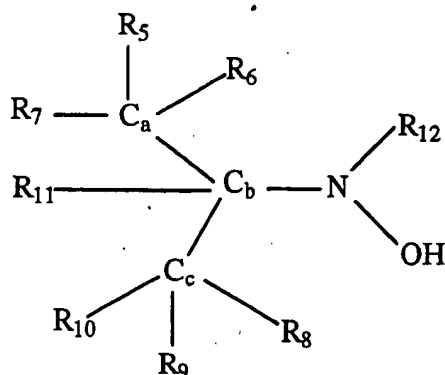
Examples of hydroxylamines according to Formula I include t-butyl hydroxylamine, 2-hydroxylamine-2-methylbutane, and 2-hydroxylamine-3-methylbutane.

Examples of substituted hydroxylamines include the following.

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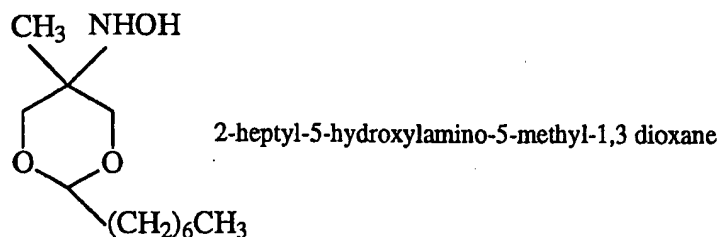


Formula II

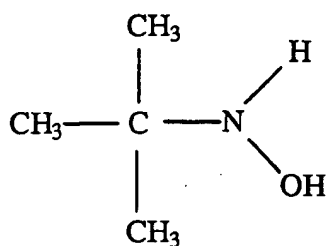


where: R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁ and R₁₂ are hydrogen or C₁-C₁₀ alkyl and two or all of C_a, C_b and C_c are included in an aliphatic or a heterocyclic ring

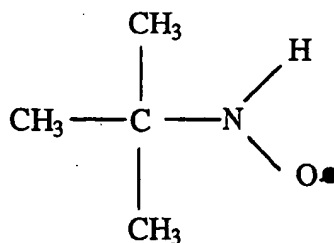
- 5 Examples of hydroxylamines according to Formula II include cycloaliphatic hydroxylamines, such as methylcyclohexyl hydroxylamine where the methyl and hydroxylamine substituents appear on the same carbon atom, and heterocyclic hydroxylamines such as the following:



- 10 The sterically-hindered hydroxylamines may form or be formed into stable nitroxides, for example, the nitroxide of t-butyl hydroxylamine



hydroxylamine



nitroxide

It is believed that the nitroxides will be effective as free radical scavengers and, thus, will serve as shortstopping agents and polymerization inhibitors.

5 Use of the Shortstops and Inhibitors

The sterically-hindered alkyl hydroxylamine is preferably added as a solution in an appropriate solvent. For example, many free radical polymerizations are carried out in an emulsion process, where it is desirable to introduce the shortstop as a relatively dilute aqueous solution. For stabilization of monomers, the solvent choice for diluting the radical scavenger will vary with the monomer. For example, ethylbenzene is a good choice for styrene, while water or another polar diluent may be preferred for acrylic acid or acrylate esters. In general, the diluted scavenger must be easily introduced into the monomer purification system using existing feed equipment, and must readily dissolve in the monomer.

Examples of polymerization systems where the present invention is applicable include, but are not limited to, free radical polymerizations of 1,3-butadiene, 2-chlorobutadiene-1,3 (chloroprene), vinyl chloride, tetrafluoroethylene, and vinylidene fluoride, as well as co-polymerizations of styrene-butadiene and acrylonitrile-butadiene. The present invention is particularly useful in shortstopping the copolymerizations of styrene-butadiene and acrylonitrile-butadiene.

20

Examples of unsaturated monomer systems where the present invention is applicable include, but are not limited to, production and purification of styrene, 1,3-butadiene, acrylonitrile, acrylic acid, methyl methacrylate, vinyl chloride, vinyl acetate, n-butyl acrylate, methyl acrylate, tetrafluoroethylene, etc. The present invention is especially useful in preventing polymerization of styrene during its production and purification.

25

In addition to the use of sterically-hindered hydroxylamines as free radical scavengers, it is believed that such hydroxylamines will also be useful as oxygen scavengers in boiler feed water treatment applications and the like. Further, combinations of the sterically-hindered hydroxylamines disclosed herein and known compounds such as TEMPO and dinitrophenols, specifically dinitro-o-sec-butylphenol, are useful free-radical scavengers.

Example 1

The usefulness of the sterically-hindered hydroxylamine t-butyl hydroxylamine (TBHA) at preventing polymerization of styrene was demonstrated in a laboratory aging test. The t-butyl catechol (TBC) inhibitor was removed from a sample of commercial styrene by passing through a TBC adsorption column. The uninhibited styrene was split into three portions. To one portion was added 500 parts per million (ppm) of active TBHA. TBHA was supplied as a 90.6 percent active solid. To a second portion was added 500 ppm active dinitro-p-cresol (DNPC). The third portion was used as a control (uninhibited). The TBHA and DNPC were dissolved by mixing, and then all of the samples were sparged with nitrogen and sealed under nitrogen in glass vials

The vials were placed into a 120°C oven for three hours, removed and cooled at room temperature for thirty minutes. The oligomer/polymer solids in each sample were measured by placing about one gram of sample into methanol and then evaporating the methanol and remaining styrene monomer in a vacuum oven at 70°C (about 16 hours). The following results were obtained.

INHIBITOR	% OLIGOMER/POLYMER SOLIDS
None	24.1
DNPC (500 ppm)	1.2
TBHA (500 ppm)	1.0

Both TBHA and DNPC are equally effective at preventing styrene polymerization. TBHA, however, is believed to be relatively safe to handle and use, while DNPC presents safety hazards as previously described.

Example 2

The efficacy of TBHA at preventing polymerization of acrylic acid was assessed in the laboratory. Commercial acrylic acid containing monomethylether hydroquinone (MEHQ) as an inhibitor was distilled. The inhibitor-free distilled material was split into two portions. To one portion was added 500 ppm of active TBHA, while the other portion served as a control (uninhibited). The samples were sealed under air and placed into an 80°C oven. The samples were checked frequently and observed for physical changes indicative of polymerization (haziness, precipitate, solidification, etc.). The elapsed time at which polymerization was first noted was recorded for each sample and the results are reported below.

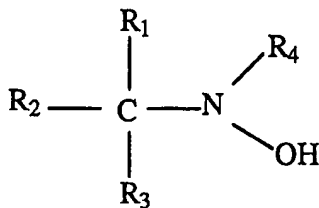
INHIBITOR	TIME BEFORE POLYMERIZATION (HOURS)
None	3
TBHA (500 ppm)	205

The results show that TBHA is very effective at delaying the onset of polymerization of acrylic acid.

While the present invention has been described with reference to one or more particular embodiments, those skilled in the art will recognize that many changes may be made thereto without departing from the spirit and scope of the present invention. Each of these embodiments and obvious variations thereof is contemplated as falling within the spirit and scope of the claimed invention, which is set forth in the following claims.

WHAT IS CLAIMED IS:

1. A free radical scavenger comprising a sterically-hindered alkyl hydroxylamine.
2. The free radical scavenger of Claim 1, wherein said sterically-hindered hydroxylamine has the formula



where R₁, R₂, R₃ and R₄ are independently hydrogen, C₁-C₁₀ alkyl, hydroxylalkyl, or amino alkyl, optionally substituted with a heterocyclic radical providing that not more than one of R₁, R₂ and R₃ may be hydrogen.

10

3. The free radical scavenger of Claim 2 wherein R₁, R₂ and R₃ are alkyl groups or hydroxyalkyl groups, and R₄ is hydrogen.

15

4. The free radical scavenger of Claim 2, wherein R₁, R₂ and R₃ are methyl and R₄ is

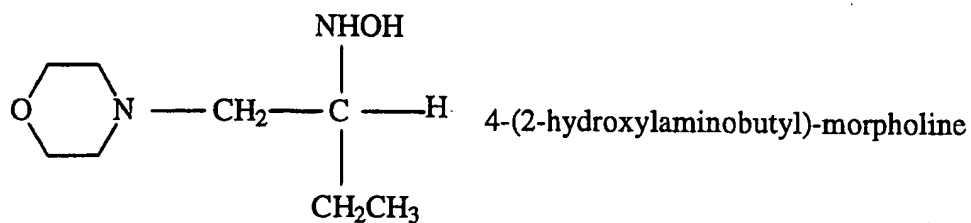
hydrogen.

5. The free radical scavenger of Claim 2, wherein R₄ is hydrogen, R₁ and R₂ are methyl, and R₃ is ethyl.

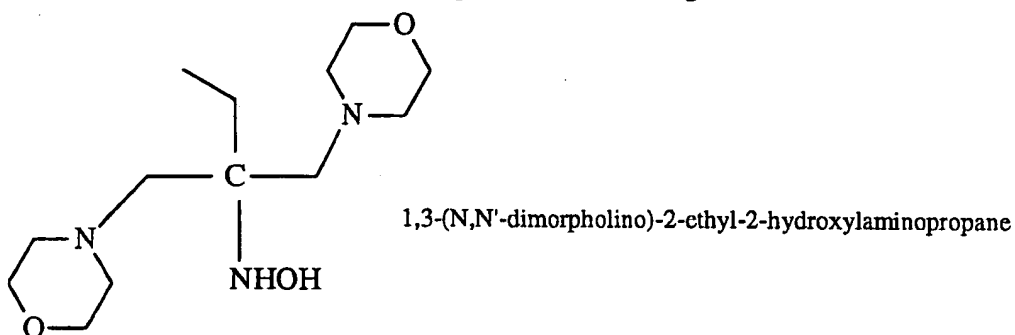
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6. The free radical scavenger of Claim 2, wherein R₁ and R₄ are hydrogen, R₂ is methyl, and R₃ is i-propyl.

7. The free radical scavenger of Claim 2 having the formula

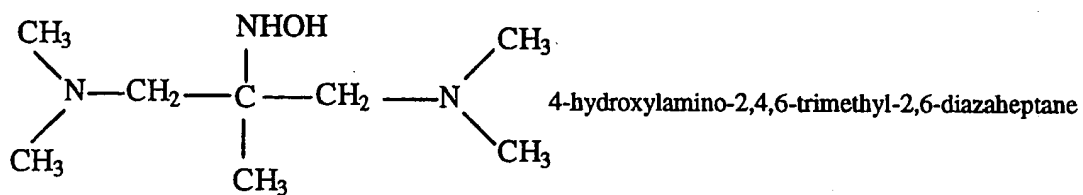


8. The free radical scavenger of Claim 2 having the formula



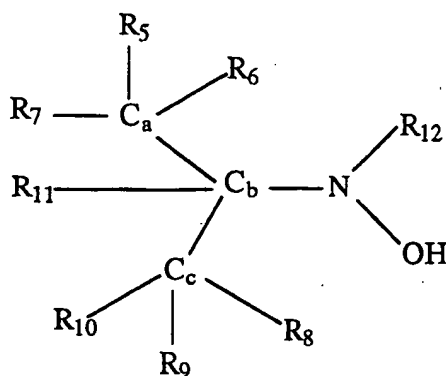
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9. The free radical scavenger of Claim 2 having the formula



10. The free radical scavenger of Claim 1, wherein said sterically-hindered hydroxylamine has the formula

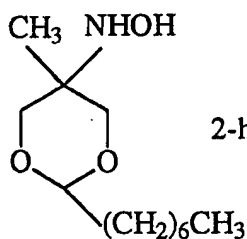
Formula II



where R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} , R_{11} and R_{12} are hydrogen or C_1 - C_{10} alkyl and two or all of C_a , C_b and C_c are included in an aliphatic or heterocyclic ring.

- 5 11. The free radical scavenger of Claim 10, wherein said cycloaliphatic ring is methylcyclohexyl.

12. The free radical scavenger of Claim 10, wherein said hydroxylamine has the formula



2-heptyl-5-hydroxylamino-5-methyl-1,3 dioxane

10

13. In a free radical polymerization reaction, the improvement comprising adding to the reacting mixture a sterically-hindered alkyl hydroxylamine as a shortstopping agent.

14. The free radical polymerization reaction of Claim 13, wherein said shortstopping agent is t-butyl hydroxylamine.
- 15

15. As a free radical polymerization inhibitor, a sterically-hindered hydroxylamine.

16. An inhibitor of Claim 15, wherein said sterically-hindered hydroxylamine is t-butyl hydroxylamine.

5 17. In a process for making a monomer which polymerizes by a free radical reaction, the improvement comprising adding a sterically-hindered hydroxylamine as a polymerization inhibitor.

18. The process of Claim 17, wherein said monomer is styrene.

10 19. The process of Claim 17, wherein said sterically-hindered hydroxylamine is t-butyl hydroxylamine

20. A method of inhibiting free radical polymerization of monomers during storage and transportation, comprising adding a sterically-hindered hydroxylamine to said monomer.

15 21. The method of Claim 20, wherein said monomer is styrene.

22. The method of Claim 20, wherein said monomer is acrylic acid.

20 23. The free radical scavenger of Claim 2 in the form of a nitroxide.

24. The free radical scavenger of Claim 10 in the form of a nitroxide.

25 25. In a process of operating a steam boiler, the improvement of adding a sterically-hindered hydroxylamine of any of Claims 1-16 as an oxygen scavenger.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/01291

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08F2/40 C08F2/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 00 14177 A (BAKER HUGHES INC) 16 March 2000 (2000-03-16) claims 1,4,10 page 1, line 20,21 page 7, line 32-35	1-6,10, 13,15, 17,18
A		11,12, 14,16, 19-22
X	EP 0 698 580 A (FABORGA SA) 28 February 1996 (1996-02-28) column 5, line 32-36	1,25
X	US 4 929 660 A (CHEN SAMUEL J) 29 May 1990 (1990-05-29) claims 1,4	1
A	column 5, line 2-35	15,17, 20,22
	-/-	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

25 May 2000

Date of mailing of the international search report

19/06/2000

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/01291

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 001 233 A (MURRAY ROBERT W ET AL) 19 March 1991 (1991-03-19)	1
A	column 2, line 3,4 examples 9,10	11
P,X	WO 99 48996 A (BETZDEARBORN INC) 30 September 1999 (1999-09-30) claims 1,3,5 page 6, line 24-26	1,15,17, 18
A	EP 0 243 936 A (DU PONT) 4 November 1987 (1987-11-04) claim 1 page 5	1,14
A	ZINNER, G. ET AL: "Hydroxylamine derivatives. 48. Reaction of N-(mono)hydroxyaminals with iso(thio)cyanates", ARCH. PHARM. (WEINHEIM) (1972), 305(1), 64-70 XP000910704	7
A	AURICH, HANS G. ET AL: "Sterically induced transformation of N-hydroxyureas and N-hydroxyguanidines", CHEM. BER. (1973), 106(6), 1881-96 XP000907017	11
A	CHEMICAL ABSTRACTS, vol. 98, no. 26, 27 June 1983 (1983-06-27) Columbus, Ohio, US; abstract no. 217615, TOKAI ELECTRO-CHEMICAL CO., LTD., JAPAN: "Stabilization of 1,1,1-trichloroethane" XP002137853 abstract & JP 58 049323 A (TOKAI ELECTRO-CHEMICAL CO., LTD., JAPAN) 23 March 1983 (1983-03-23)	1,12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/01291

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 0014177	A	16-03-2000	NONE		
EP 0698580	A	28-02-1996	AT 144968 T		15-11-1996
			DE 59401005 D		12-12-1996
US 4929660	A	29-05-1990	NONE		
US 5001233	A	19-03-1991	NONE		
WO 9948996	A	30-09-1999	US 6024894 A		15-02-2000
EP 0243936	A	04-11-1987	AU 7223787 A		05-11-1987
			CA 1333537 A		20-12-1994
			DE 3777231 A		16-04-1992
			JP 1733531 C		17-02-1993
			JP 4018293 B		27-03-1992
			JP 62267736 A		20-11-1987
JP 58049323	A	23-03-1983	JP 1222100 C		15-08-1984
			JP 58052967 B		26-11-1983